II.B.12 Production and Storage of Hydrogen from Coal Using C1 Chemistry

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Objectives

- Develop novel approaches to produce hydrogen from coal with "breakthrough technology" potential.
- Develop new materials with potential to solve the very difficult problem of hydrogen storage.
- Explore catalytic dehydrogenation of hydrogen-rich carrier liquids as an alternative to reforming.

Introduction

The Consortium for Fossil Fuel Science (CFFS) is a multi-university research consortium with participants from the Universities of Kentucky, West Virginia, Pittsburgh, Utah, and Auburn. The proposed three-year research program is focused on: (1) developing novel processes for the production of hydrogen using C1 chemistry, (2) developing novel hydrogen storage materials, and (3) synthesis and dehydrogenation of hydrogen-rich carrier liquids. The feedstocks include synthesis gas derived from coal, gaseous and liquid hydrocarbons produced from coal-derived syngas, coalbed methane, and natural gas.

The primary objectives of this effort are:

1. Develop novel approaches to produce hydrogen from coal with “breakthrough technology” potential.
2. Develop new materials with potential to solve the very difficult problem of hydrogen storage.
3. Explore catalytic dehydrogenation of hydrogen-rich carrier liquids as an alternative to reforming.

Approach

Experimental results and equilibrium calculations show that high reaction temperature is favorable for H_2 production, and low temperature improves methane production and selectivity. Among the catalysts we have tested, Cu/MgO exhibits the highest H_2 production but has low methane production and selectivity. Cu/TiO_2 catalyst has high methane production and selectivity but low H_2 production, while Cu/Al_2O_3 catalyst has very low methane production and selectivity with high amounts of dimethyl ether, probably due to the acidic nature of the support. Cu/ZrO_2 is the most effective for co-production of H_2 and methane at temperatures between 240°C and 260°C; this catalyst shows high promise and is being more thoroughly investigated.

In this project, the reforming of methanol is carried out in supercritical water at 276 bar and 700°C to produce H_2 along with CO, CH_4 and CO_2. The reactions are catalyzed by the wall of the tubular reactor made of Inconel 600 which is an alloy of Ni, Cr and Fe. Experiments are conducted to study the effect of pressure, residence time and steam-to-carbon ratio on the H_2 yield. The residence time is varied by changing the length of reactor as well as feed flow rate. Both the experimental results and equilibrium calculations show that as pressure increases, methanation of CO and CO_2 takes place resulting in a loss H_2. In addition, methane formation is favored at a high residence time and low steam-to-carbon ratio. In this study the following three strategies are proposed for the suppression of methane formation during the production of H_2 from methanol in supercritical water: (1) operation at a low residence time by having small reactor length or high feed flow rate (2) addition of a small amount of K_2CO_3 or KOH in the feed, and (3) utilization of the surface catalytic activity of the reactor made of Ni-Cu alloy. These three strategies resulted in a significant reduction in methane formation and an enhancement in H_2 production.

Accomplishments

- Developed new continuous methods of producing a high hydrogen content gas by reforming C1 compounds in supercritical water.
- Developed a process to produce hydrogen and chemicals via dehydrogenation of methanol for formaldehyde and subsequent reactions.
- Developed novel bimetallic carbide catalysts for the steam reforming of methanol.

Future Directions

- Hold meeting to present research results and obtain program/project direction.
- Build a continuous reactor for the catalytic dehydrogenation of light alkanes to produce pure hydrogen and carbon nanotubes using unsupported, iron-based, nanoparticle catalysts.

FY 2006 Publications/Presentations

1. Gadhe, Jayant B.; Gupta, Ram B., Hydrogen Production from Methanol in Supercritical Water. Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2005), 50(2), 604-605.

2. Gadhe, Jayant B.; Gupta, Ram B., Hydrogen Production by Methanol Reforming in Supercritical Water: Suppression of Methane Formation. Industrial & Engineering Chemistry Research (2005), 44(13), 4577-4585.

3. F. Shi, Y. Zhang, J. W. Tierney and I. Wender, "Co-production of Hydrogen and Chemicals by Vapor Phase Decomposition of Methanol", Am. Chem. Soc., Div. Fuel Chem. 2005, 50 (2).